Reference: Moffat, I., Stringer, C., and Grun, R., 2012, Spatially resolved LA-MC-ICPMS strontium isotope microanalysis of archaeological fauna, *Palaios*, 27(9): 667-670.

Title: Geophysical prospection for late Holocene burials in coastal environments: Possibilities and problems from a pilot study in South Australia

Authors: Ian Moffat, Chris Stringer and Rainer Grün

The analysis of the strontium isotope composition of archaeological materials can provide important information about the mobility of a range of mammals, including humans. The basis of this method is that, prior to any postburial diagenesis, the Sr87/Sr86 ratio of bone and teeth reflects the geological environment from which food and water were sourced while these biominerals were forming. Teeth are particularly amenable to tracing the geographic origins of humans as they mineralize during the first 12–13 years of life (White and Folken, 2005) and do not subsequently change strontium composition after this time (Schweissing and Grupe, 2003). Strontium isotope analysis can be used to determine if individuals are local or nonlocal by comparison to the isotopic composition in and around their burial location (i.e., Schweissing and Grupe, 2000; Bentley et al., 2007; Conlee et al., 2009). In order to quantify the extent of faunal mobility, the strontium isotope composition of biominerals from fossil samples needs to be compared with a regional map of values obtained either from local faunal material (Price et al., 2002) or from analysis of the bioavailable component of strontium from plants, regolith, or bedrock (Capo et al., 1998).

Strontium isotope analysis has been extensively applied to the determination of archaeological mobility, as reviewed by Price et al. (2002), Budd et al. (2004), Bentley (2006), and Montgomery (2010). Although studies of Paleolithic or older archaeological material are rare, some have been undertaken on hominins (Sillen et al., 1995, 1998; Richards et al., 2008; Copeland et al., 2011) and faunal material (Horn et al., 1994; Copeland et al., 2010; Britton et al., 2011).

Enamel has been shown to be the most favorable material for strontium isotope analysis based on its ability to resist postburial alteration far better than dentine, cement, or bone (Trickett et al., 2003). Enamel of some species grows over extended periods and, when analyzed with microprofiling or laser ablation analysis, can be used to reconstruct comprehensive life histories. This approach demonstrated the seasonal mobility of cattle in Iron Age Britain (Horstwood et al., 2008), Neolithic Germany (Bentley and Knipper, 2005), and England (Viner et al., 2010).

Traditionally, strontium isotope ratios have been analyzed by mechanically removing and dissolving the material of interest, undertaking ion exchange chromatography to separate strontium from other matrix elements, and measuring the relative isotope abundance using thermal ionization mass spectrometry. New advances in instrumentation, in particular laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICPMS), provide considerable advantages over traditional techniques as they offer: (1) high spatial resolution (50–100 μm); (2) faster analysis time; (3) less damage to the samples (Horstwood et al., 2008, p. 5659); (4) direct characterization of solids; (5) no chemical dissolution; (6) reduced risk of contamination; and (7) spatial distribution of results within a sample (Russo et al., 2002). The development of He ablation cells has allowed the size of the analysis spot to be further reduced to 10 μm , due to the increased transport efficiency away from the ablation site compared to Ar (Eggins et al., 1998). One potential disadvantage is a possible Ca+P+O isobaric interference on mass 87 that may lead to an offset between solution and laser analysis results at low strontium concentrations (Horstwood et al., 2008; Simonetti et al., 2008), although this approach is still valid in appropriate circumstances (Copeland et al., 2008).

In a forthcoming study, we present the results of LA-MC-ICPMS analysis of a range of faunal material from early–middle Paleolithic archaeological sites in Israel and southern France. These results are compared to data from an extensive program of soil, rock, and plant analysis to quantify mobility. These sites, which include Amud, Qafzeh, Tabun, Skhul, Holon, Bois Roche, Le Moustier, La Chapelle-aux-Saints, Les Fieux, Pech del'Aze II, and Rescoududou, range in age from Marine Isotope Stages 9 to 3, i.e., between ca. 334 ka and 60 ka. The sites contained archaeological material attributed to *Homo heidelbergensis*, *Homo neanderthalensis*, and anatomically modern humans. Of particular interest within the study area is the early presence of anatomically modern humans in Israel, who made a precocious and apparently short-lived incursion into the region ahead of their later global radiation from Africa ca. 60 ka (Endicott et al., 2009).

While a comprehensive discussion of our findings is beyond the scope of this paper, we present the results from sample 852, a bovid molar from the archaeological site of Skhul in the Mount Carmel region of Israel (Fig. 1). Our purpose is to illustrate how the Sr87/Sr86 ratio of a bovid tooth can be used as a proxy record for the mobility of an individual across a landscape.

The site of Skhul is a small cave with a large associated terrace, located in a small valley approximately 20 km south of Haifa. The site was the subject of a test excavation in 1929 by Kitson-Clark before substantial excavations in 1931 and 1932 by McCown (1932, 1933). The site contained at least 10 hominins as well as isolated fragments of skeletal material (McCown and Keith, 1939). These have been classified as anatomically modern humans (Stringer, 2002) although some workers claim a meaningful overlap with the Neanderthal range (Kramer et al., 2001). The site of Skhul, which is located on Yagur-Kammon Formation dolostone (Albian–Cenomanian), is immediately to the east of Quaternary coastal sediments and kurkar ridges (cemented eolian dunes), and is near several faulted, Upper Cretaceous igneous outcrops including undifferentiated basalt, gabbro, and ultramafic pyroclastic strata (Sneh et al., 1998).

A bovid tooth, previously directly dated using electron spin resonance in the range of between 61 $\pm$ 8 ka (early uptake) and 77 $\pm$ 11 ka (linear uptake) (Gruen et al., 2005), was sequentially analyzed for relative strontium isotope abundance using LA-MC-ICPMS along the growth axis of the tooth, with 42 and 39 analysis spots in the dentine and enamel, respectively (Fig. 1). This

tooth was originally excavated from the site during the McCown excavation. Unfortunately, no precise stratigraphic information was recorded concerning its exact provenience.

With the exception of analysis spots one and two, which we consider sample collection artifacts, the enamel Sr87/Sr86 values of this bovid molar vary rhythmically from a domain of values of ,0.7085 to a domain of values of ,0.7109, as shown in Figure 2. This variation probably represents regular mobility between two distinct geological environments by the individual (from which this specimen was taken) during the period of enamel formation. As bovid molars continue to form after birth over a period of ,12 months (Brown et al., 1960), this would represent a subannual mobility between different geological environments.

Analysis of soil Sr87/Sr86 values from the coastal plain (0.7089– 0.7095) and carbonate highlands of the Mount Carmel Range (0.7081– 0.7087) show some correlation with the two principal domains of enamel Sr87/Sr86 values from sample 852. These values broadly correlate with the domains found within the bovid enamel, although the more radiogenic enamel domain of 0.7109 is slightly elevated compared with the values from the coastal plain. The most parsimonious explanation is that this is the result of a Ca+P+O isobaric interference on mass 87 that, given the Sr concentration in this sample (277 ppm), would increase the Sr87/Sr86 ratio in the enamel (Horstwood et al., 2008).

Figure 1 —Bovid molar 852 from the archaeological site of Skhul, Israel.

Figure 2 — $\text{Sr}^{87}/\text{Sr}^{86}$ LA-MC-ICPMS results from bovid molar 852.

Conclusions

In summary, the strontium isotope results obtained from this bovid molar with LA-MC-ICPMS demonstrate multiannual mobility during amelogenesis—the formation of enamel on teeth during the crown stage of tooth development. Assuming a contribution from $\text{Ca}+\text{P}+\text{O}$ isobaric interference, this animal most likely regularly moved between the coastal plain and the Mount Carmel elevated region. To obtain a similar number of data points using traditional strontium isotope methods would have required an excessive amount of laboratory and instrument time. While improvements to LA-MC-ICPMS techniques for materials with such relatively low strontium concentration as enamel are required, this approach demonstrates significant potential as a means of developing a nuanced understanding of archaeological mobility.

Acknowledgements

This research was supported by Australian Research Council grants DP0664144 and DP110101415 to Gruen et al. Chris Stringer is a member of the Ancient Human Occupation of Britain project, funded by the Leverhulme Trust, and his work is also supported by the Human Origins Research Fund (NHM) and the Calleva Foundation. Thank you to Graham Mortimer, Les Kinsley, Linda McMorro, Max Aubert, Steve Eggins, Malte Willmes, Liora Koska Horwitz, and Avraham Ronen for assistance during fieldwork and analysis.

References

BENTLEY, R.A., 2006, Strontium isotopes from the Earth to the archaeological skeleton: A review: *Journal of Archaeological Method and Theory*, v. 13, no. 3, p. 135–187.

BENTLEY, R.A., and KNIPPER, C., 2005, Transhumance at the early Neolithic settlement at Vaihingen (Germany): *Antiquity*, v. 79, <http://www.antiquity.ac.uk/projgall/bentley306/>. Checked September 2012.

BENTLEY, R.A., TAYLES, N., HIGHAM, C., MACPHERSON, C., and ATKINSON, T.C., 2007, Shifting gender relations at Khok Phanom Di, Thailand: *Current Anthropology*, v. 48, no. 2, p. 301–314.

BRITTON, K., GRIMES, V., NIVEN, L., STEELE, T.E., MCPHERRON, S., SORESSI, M., KELLY, T.E., JAUBERT, J., HUBLIN, J.-J., and RICHARDS, M.P., 2011, Strontium isotope evidence for migration in late Pleistocene *Rangifer*: Implications for Neanderthal hunting strategies at the middle Palaeolithic site of Jonzac, France: *Journal of Human Evolution*, v. 61, no. 2, p. 176–185.

BROWN, W.A.B., CHRISTOFFERSON, P.V., MASSLER, M., and WEISS, M.B., 1960, Postnatal tooth development in cattle: *American Journal of Veterinary Research*, v. 21, no. 80, p. 7–34.

BUDD, P., MILLARD, A., CHENERY, C., LUCY, S., and ROBERTS, C.A., 2004, Investigating population movement by stable isotope analysis: A report from Britain: *Antiquity*, v. 78, no. 299, p. 127–141.

CAPO, R.C., STEWART, B.W., and CHADWICK, O.A., 1998, Strontium isotopes as tracers of ecosystem processes: Theory and methods: *Geoderma*, v. 82, no. 1–3, p. 197–225.

CONLEE, C.A., BUZON, M.R., GUTIERREZ, A.N., SIMONETTI, A., and CREASER, R.A., 2009, Identifying foreigners versus locals in a burial population from Nasca, Peru: An investigation using strontium isotope analysis: *Journal of Archaeological Science*, v. 36, no. 12, p. 2755–2764.

COPELAND, S.R., SPONHEIMER, M., LE ROUX, P.J., GRIMES, V., LEE-THORP, J.A., DE RUITER, D.J., and RICHARDS, M.P., 2008, Strontium isotope ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) of tooth

enamel: A comparison of solution and laser ablation multicollector inductively coupled plasma mass spectrometry methods: *Rapid Communications in Mass Spectrometry*, v. 22, p. 3187–3194.

COPELAND, S.R., SPONHEIMER, M., LEE-THORP, J.A., LE ROUX, P.J., DE RUITER, D.J., and RICHARDS, M.P., 2010, Strontium isotope ratios in fossil teeth from South Africa: Assessing laser ablation MC-ICP-MS analysis and the extent of diagenesis: *Journal of Archaeological Science*, v. 37, no. 7, p. 1437–1446.

COPELAND, S.R., SPONHEIMER, M., DE RUITER, D.J., LEE-THORP, J.A., CODRON, D., LE ROUX, P.J., GRIMES, V., and RICHARDS, M.P., 2011, Strontium isotope evidence for landscape use by early hominins: *Nature*, v. 474, no. 7349, p. 76–78.

EGGINS, S.M., KINSLEY, L.P.J., and SHELLEY, J.M.G., 1998, Deposition and element fractionation processes during atmospheric pressure laser sampling for analysis by ICP-MS: *Applied Surface Science*, v. 127–129, p. 278–286.

ENDICOTT, P., HO, S., METSPALU, M., and STRINGER, C., 2009, Evaluating the mitochondrial timescale of human evolution: *Trends in Ecology and Evolution*, v. 24, p. 515–521.

GRUÑIN, R., STRINGER, C., MCDERMOTT, F., NATHAN, R., PORAT, N., ROBERTSON, S., TAYLOR, L., MORTIMER, G., EGGINS, S., and MCCULLOCH, M., 2005, U-series and ESR analyses of bones and teeth relating to the human burials from Skhul: *Journal of Human Evolution*, v. 49, no. 3, p. 316–334.

HORN, P., HÖLZL, S., and STORZER, D., 1994, Habitat determination on a fossil stag's mandible from the site of *Homo erectus heidelbergensis* at Mauer by use of $^{87}\text{Sr}/^{86}\text{Sr}$: *Naturwissenschaften*, v. 81, no. 8, p. 360–362.

HORSTWOOD, M.S.A., EVANS, J.A., and MONTGOMERY, J., 2008, Determination of Sr isotopes in calcium phosphates using laser ablation inductively coupled plasma mass spectrometry and their application to archaeological tooth enamel: *Geochimica et Cosmochimica Acta*, v. 72, no. 23, p. 5659–5674.

KRAMER, A., CRUMMETT, T.L., and WOLPOFF, M.H., 2001, Out of Africa and into the Levant: Replacement or admixture in Western Asia?: *Quaternary International*, v. 75, p. 51–63.

MCCOWN, T.D., 1932, A note on the excavation and the human remains from the Mugharet Es-Sukhul (Cave of the Kids), season of 1931: Bulletin of the American School of Prehistoric Research, v. 8, p. 12–15.

MCCOWN, T.D., 1933, Fossil men of the Mugharet Es-Sukhul, near Athlit, Palestine, season of 1932: Bulletin of the American School of Prehistoric Research, v. 9, p. 9–15.

MCCOWN, T.D., and KEITH, A., 1939, The Stone Age of Mount Carmel: The Fossil Human Remains from the Levalliso-Mousterian: Clarendon Press, Oxford, UK, 390 p.

MONTGOMERY, J., 2010, Passports from the past: Investigating human dispersals using strontium isotope analysis of tooth enamel: Annals of Human Biology, v. 37, no. 3, p. 325–346.

PRICE, T.D., BURTON, J.H., and BENTLEY, R.A., 2002, The characterization of biologically available strontium isotope ratios for the study of prehistoric migration: Archaeometry, v. 44, no. 1, p. 117–135.

RICHARDS, M.P., HARVATI, K., GRIMES, V., SMITH, C., SMITH, T., HUBLIN, J.J., KARKANAS, P., and PANAGOPOULOU, E., 2008, Strontium isotope evidence of Neanderthal mobility at the site of Lakonis, Greece using laser-ablation PIMMS: Journal of Archaeological Science, v. 35, p. 1251–1256.

RUSSO, R.E., MAO, X., LIU, H., GONZALEZ, J., and MAO, S.S., 2002, Laser ablation in analytical chemistry: A review: Talanta, v. 57, no. 3, p. 425–451.

SCHWEISSING, M.M., and GRUPE, G., 2000, Local or nonlocal? A research of strontium isotope ratios of teeth and bones on skeletal remains with artificial deformed skulls: Anthropologischer Anzeiger; Bericht u'ber die biologisch-anthropologische Literatur, v. 58, no. 1, p. 99–103.

SCHWEISSING, M.M., and GRUPE, G., 2003, Tracing migration events in man and cattle by stable strontium isotope analysis of appositionally grown mineralized tissue: International Journal of Osteoarchaeology, v. 13, p. 96–103.

SILLEN, A., HALL, G., and ARMSTRONG, R., 1995, Strontium calcium ratios (Sr/Ca) and strontium isotopic ratios ($^{87}\text{Sr}/^{86}\text{Sr}$) of *Australopithecus robustus* and *Homo* sp. from Swartkrans: *Journal of Human Evolution*, v. 28, no. 3, p. 277–285.

SILLEN, A., HALL, G., RICHARDSON, S., and ARMSTRONG, R., 1998, $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in modern and fossil food-webs of the Sterkfontein Valley: Implications for early hominid habitat preference: *Geochimica et Cosmochimica Acta*, v. 62, no. 14, p. 2463–2473.

SIMONETTI, A., BUZON, M.R., and CREASER, R.A., 2008, In-situ elemental and Sr isotope investigation of human tooth enamel by laser ablation-(MC)-ICP-MS: Successes and Pitfalls: *Archaeometry*, v. 50, p. 371–385.

SNEH, A., BARTOV, Y., and ROSENSAFT, M., 1998, Geological Map of Israel, 1:200,000, Sheet 1: Geological Survey of Israel.

STRINGER, C., 2002, Modern human origins: Progress and prospects: *Philosophical Transactions of the Royal Society, London (B)*, v. 357, p. 563–579.

TRICKETT, M.A., BUDD, P., MONTGOMERY, J., and EVANS, J., 2003, An assessment of solubility profiling as a decontamination procedure for the $^{87}\text{Sr}/^{86}\text{Sr}$ analysis of archaeological human skeletal tissue: *Applied Geochemistry*, v. 18, no. 5, p. 653–658.

VINER, S., EVANS, J., ALBARELLA, U., and PEARSON, M.P., 2010, Cattle mobility in prehistoric Britain: Strontium isotope analysis of cattle teeth from Durrington Walls (Wiltshire, Britain): *Journal of Archaeological Science*, v. 37, no. 11, p. 2812–2820.

WHITE, T.D., and FOLKENS, P.A., 2005, *The Human Bone Manual*: Elsevier Academic Press, Amsterdam, 464 p.